INTRODUCTION

The phase behavior of polymer blends has become a topic of major scientific investigation during the past decade because of fresh insights into the issues involved and because of intensified technological interest in multicomponent polymer systems. The purpose here is to review the basic thermodynamic principles involved in polymer-polymer miscibility and to introduce some of the simpler methods for quantifying the interaction between the components which is a major factor. This will form a framework for developing relationships between blend phase behavior and the molecular structure of the component polymers. The approach will be restricted to classical theories of the Flory-Huggins type and to simple physical techniques which are generally available in most research laboratories. Subsequent chapters will deal with the newer and more advanced theories as well as sophisticated experimental techniques like neutron scattering. The utility and limitations of the solubility parameter as a means predicting phase behavior will be outlined briefly.

Several monographs and reviews (1-18) are available for further study.

GENERAL ASPECTS OF PHASE BEHAVIOR

Blends of two or more different polymers may exist in a completely homogeneous state where their segments are mixed at the most intimate level or they may segregate into distinct
Phases. Phase segregation may be the result of incomplete miscibility between two fluid or molten polymers or it may be caused by crystallization of one or more components from an otherwise homogeneous melt mixture. Obviously, both modes of phase segregation may exist simultaneously. A homogeneous amorphous phase upon cooling will eventually become a glass at a single temperature intermediate between the glass transitions of the pure components. The glass transition of the blend will depend on composition and reflect the mixed environment of the segments. This will be so even if phase segregation by crystallization has occurred provided there remains a homogeneous amorphous phase albeit of a different composition than the overall blend. On the other hand, blends comprised of separate amorphous phases will exhibit glass transitions characteristics of each phase. Thus, glass transition behavior can be a powerful tool for identifying the amorphous phase structure of blends as seen in subsequent chapters.

Homogeneous blends may experience liquid-liquid phase separation as the result of either raising or lowering the temperature (19) as suggested in Fig. 1. Generally, UCST behavior is characteristic of systems which mix endothermically while LCST behavior is characteristic of exothermic mixing and associated entropy effects. LCST behavior is rather common in polymer blends while UCST behavior is usually limited to cases where miscibility is the result of the low molecular weight of the components, e.g. mixtures of oligomers. In general, liquid-liquid phase equilibrium results in the presence of both components to some extent in each phase although this can be very limited in polymer blends. Because of partial miscibility,

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**Figure 1.** Liquid-liquid phase behavior for binary mixtures illustrating systems with an upper critical solution temperature (left) and a lower critical solution temperature (right). (By permission of the MMI Press. Copyright 1982.)